Starner

Action of Oxidizing agents on Coal

ACTION OF OXIDIZING AGENTS ON COAL

BY

VERNER STARNER

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMISTRY

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1917

UNIVERSITY OF ILLINOIS

Febr. 27, 1917

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Verner Starner

ENTITLED Action of Oxidizing Agents on Coal.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemistry

H. J. Broderson
Instructor in Charge

APPROVED: W. A. Noyes

HEAD OF DEPARTMENT OF Chem

Table of Contents.

Introduction.

The weathering and spontaneous combustion of coal are dependent upon the contact of the coal with oxygen or air.The weathering of coal is said to begin the very moment that it is exposed to air in the mine. Coal stored in bins for long periods of time has often been known to ignite due to the heat produced by the absorption of oxygen.

F.E.E. Lamplough and A. Muriel Hill (1) have recently carried on a series of investigations in England regarding the nature of the chemical changes involved in the slow combustion of coal dust. They found that the heat evolved when coal dust was heated in an atmosphere rich in oxygen was nearly proportional to the volume of oxygen absorbed, the mean value being 3.3 calories of heat produced during the oxidation brought about by the absorption of one cubic centimeter of oxygen. The production of heat they attributed to two chemical changes, the oxidation of iron pyrite and the oxidation of carbonaceous matter. The oxidation of coal dust takes place in contact with gas containing much less oxygen than the normal proportion of oxygen present in air.

S.W. Parr and W.A. Wheeler (2) at the University of Illinois have carried on a series of experiments regarding the changes which occurred in coal under different conditions of storage. They found that changes in weight occurred which may be either gains or losses, probably never over two percent in a period of one year. The heating value decreases most rapidly during the first week after mining and continues to decrease more and more slowly for an indefinite time, one

[illegible]

per cent being about the average loss for the first week and three and one half per cent would cover the losses for a year.

David White (3) in his study of the effect of oxygen in coal has shown that weathered coal always has a lower heating value than freshly mined coal. By the analysis of samples collected near the foot of the shaft and those collected near the surface of the ground, Mr. White has found that the difference in the heating values may be as much as 624 calories.

Horace C. Porter and O. C. Ralston (4) have made a careful study of the oxidation of coal with special reference to the factors influencing the rate of oxidation of coal. They found that temperature and pressure had a marked effect upon the rate of oxidation.

The work about to be described here was taken up with the object in view of ascertaining the effect of oxidizing solutions on coal and to see if the subjection of coal to oxygen under high pressures would produce the same effects as those produced by weathering over long periods of time.

Experimental.

I. The Treatment of Coal with Iodine Solutions.

The method of experimental work is very similar to that used by Dr. Hart (5) in his work on the treatment of English coals with iodine solutions. A sample of coal was obtained from a car standing on the tracks at the University Power House. It was air dried and powdered to 60 and 100 mesh

respectively. Five tenths gram samples were used in most all cases. The coal was permitted to stand in an excess of tenth normal iodine solution for two hours. It was then filtered into a gooch crucible and washed with water and chloroform until the washings showed no test for iodine with starch solution. The amount of iodine taken up by the coal was determined by titrating the filtrate with tenth normal sodium thiosulphate solution.

Table I.-- The amount of iodine taken up by coal powdered to 60 and 100 mesh respectively.

Sample	Weight of Sample	Mesh	Temp.	Time	cc. of N/10 Iodine added	Normal cc. of Iodine taken up by the coal	Iodine taken up in grams	Per Cent	"O" Equiv in grams
1	.5	60	Room	2hr.	10	.1538	.0195	3.9	.00122
2	.5	60	"	"	10	.1518	.0192	3.85	.00121
3	.5	100	"	"	15	.3575	.0454	9.08	.00286
4	.5	100	"	"	15	.3518	.0446	8.94	.00280
5	.5	100	"	"	25	.3538	.0459	9.18	.00289
6	.5	100	"	"	25	.3939	.0500	10	.00310
7	.5	100	"	"	25	.4318	.0548	10.96	.00345

It was thought advisable to treat several samples of gas coke ground to pass the same mesh as the coal and compare the amount of iodine taken up with that taken up by the coal. The coke was treated in exactly the same manner as the coal.

[illegible]

[illegible]

[illegible]

[illegible]

Table II.-- The amount of iodine taken up by samples of gas coke.

Sample	Weight of Sample	Mesh	Temp	Time	cc. of N/10 Iodine added	N cc. of I taken up.	Gms. of Iodine taken up	Per Cent	O Equiv. in grams
1	.5	30	Room	2hr.	15	.0986	.0125	2.50	.00078
2	.5	30	"	"	15	.1145	.0145	2.91	.00091
3	.5	100	"	"	15	.4009	.0509	10.18	.0032
4	.5	100	"	"	15	.4103	.0521	10.42	.0033

A series of determinations was carried out on the same coal ground to pass a 200 mesh sieve and varying the concentrations of the iodine solutions and the time which the coal remained in contact with them.

Table III.-- The amount of iodine taken up by the coal when treated with .04 N iodine solution.

Sample	Weight of Sample	Time in days	Temp.	cc. of solution added	N. cc. of iodine taken up	Grams of iodine taken up	Per Cent	Oxygen Equiv. in grams
1	.5	1	Room	50	.8287	.1052	21.04	.0066
2	.5	2	"	50	1.08	.1371	27.42	.00863
3	.5	3	"	50	1.06	.1346	26.92	.00848
4	.5	5	"	50	1.19	.1511	30.22	.00951
5	.5	6	"	50	1.25	.1587	31.75	.00999
6	.5	7	"	50	1.28	.1625	32.51	.0102
7	.5	10	"	50	1.31	.1663	33.27	.0104
8	.5	30	"	50	1.46	.1854	37.08	.0116

The following curve (pg.6) is obtained by plotting the time in days as ordinates and the number of c.c. of iodine taken up by the coal as abscissa.

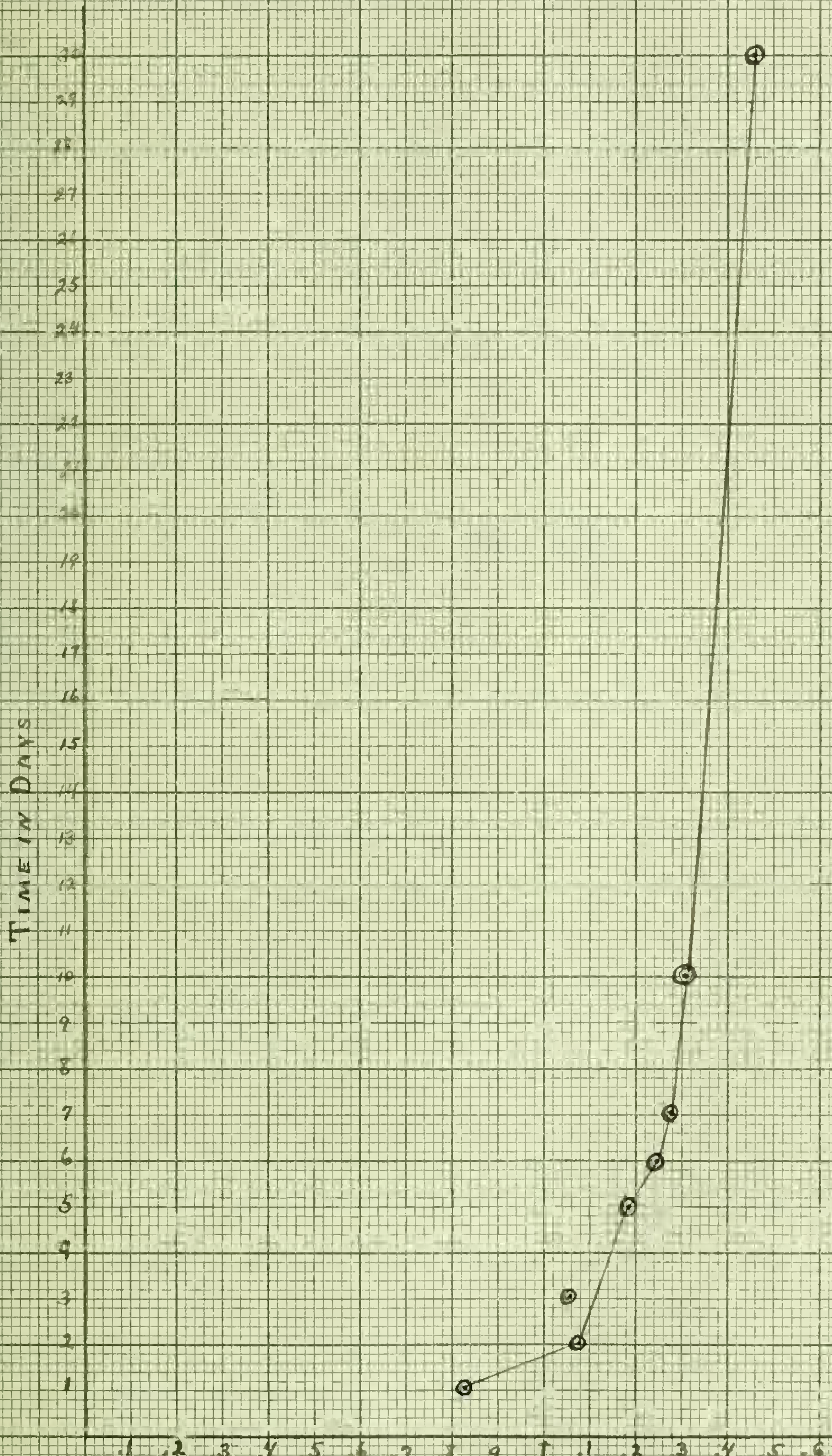
Table IV.-- The amount of iodine taken up by the coal when treated with N/10 iodine solution.

Sample	Wgt. of Sample	Time in days	Normality	Amt. added	c.c. N.I. taken up	Iodine in grams	Per Cent	O Equiv. in grams
1	.5	1	1/10	25	1.204	.1529	30.58	.00963
2	.5	2	"	25	1.301	.1652	33.04	.0104
3	.5	3	"	25	1.37	.1739	34.79	.0109
4	.5	5	"	25	1.71	.2171	43.43	.0133
5	.5	6	"	25	1.66	.2108	42.16	.0132
6	.5	7	"	25	1.58	.2006	40.13	.0125
7	.5	10	"	25	1.60	.2032	40.64	.0128
8	.5	30	"	50	2.62	.3337	66.74	.0209

The curve showing the relation between the amount of iodine taken up and the time when 1/10 normal iodine solution is used is given on page 7.

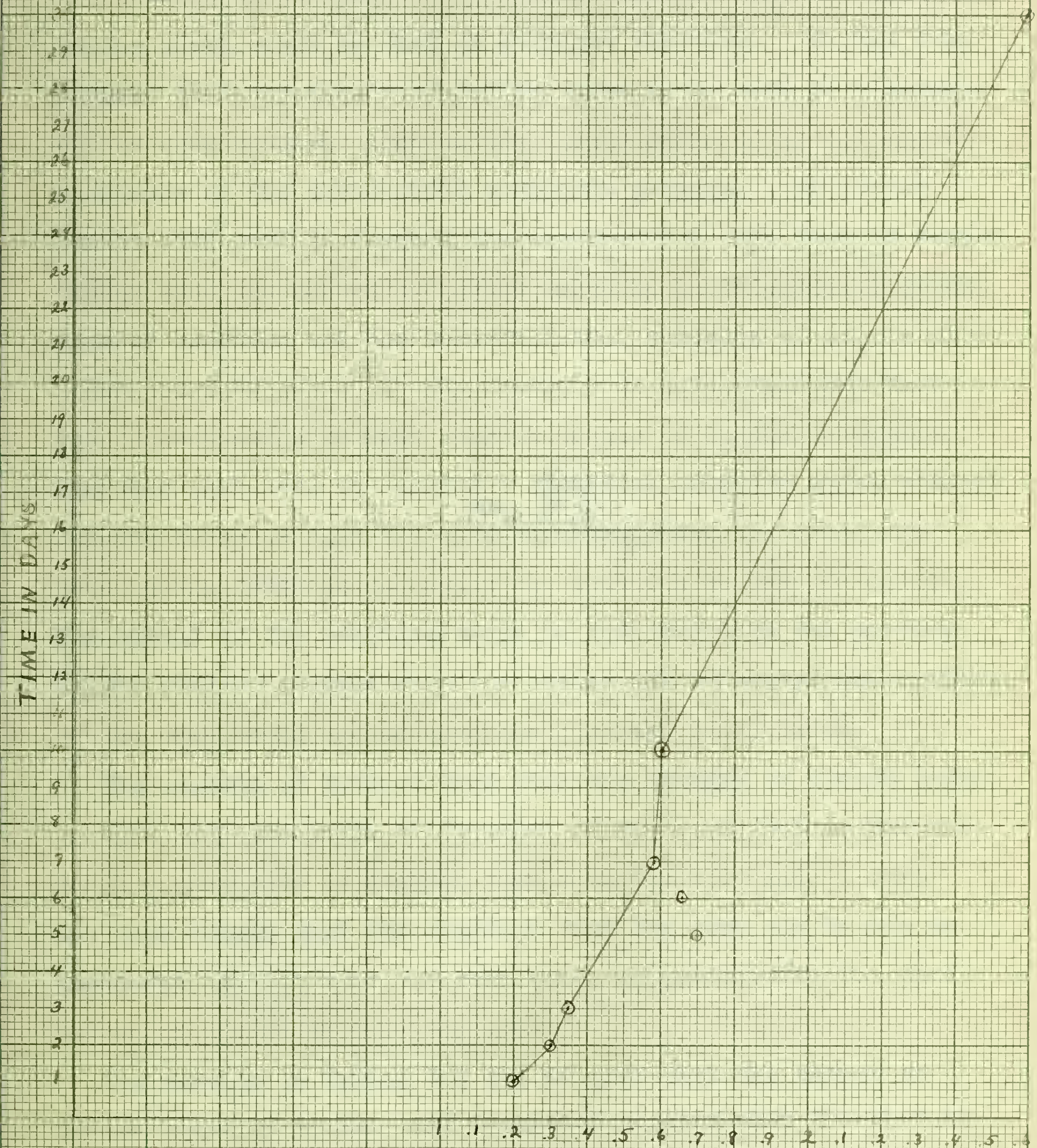
A glance at tables III and IV shows ~~that~~ the amount of iodine taken up by the coal to be dependent upon the time of contact and the concentration of the solution.

Curve showing the relation between the time of contact and the number of cubic centimeters of iodine taken up by the coal when treated with .04 normal iodine solution.



cubic centimeters of Normal Iodine taken up by the coal.

Curve showing the relation between the amount of iodine taken up and the time of contact when coal is treated with N/10 iodine solution.



cubic centimeters of Normal Iodine taken up by the coal.

The reaction between iodine and coal may be either adsorption, oxidation or substitution. If any unsaturated compounds are present in the coal it is likely that one type of oxidation taking place would be that of straight addition. It has been thought that the amount of iodine taken up by coal is a measure of the unsaturation, just as the iodine value of an oil may be a measure of the unsaturated compounds present. If iodine reacts with coal to destroy the unsaturation only then it should follow that the amount of iodine taken up be independent of the time of reaction and the concentration, assuming of course that a few hours be given for the reaction to take place and that the concentration is such that an excess of iodine is present. The fact that coal is insoluble in iodine solution might account for the evidence that the more finely divided the coal, the more iodine taken up and still the reaction be one of addition The extent of the reaction would be determined by the surface of the coal in contact with the iodine and of course the surface of the coal would depend upon the fineness of division.

The results of Table I show that the amounts of iodine taken up vary with the state of division of the coal, but in TableII we find that this is equally true with the coke and it does not seem likely that the reaction with the coke can be due to unsaturation. In fact the coke takes up practically the same amount of iodine as does the coal.

The results in Tables III and IV show that the amount of iodine taken up by the coal increases rapidly with the time it

is in contact with the coal. These results also are consistent with those in Tables I and II in so far as the amount of iodine taken up varies with the concentration.

More consistent results were obtained by using Hanus iodine solution instead of the aqueous. The solution was prepared by dissolving thirteen grams of iodine in one liter of glacial acetic acid and adding enough bromine to double the halogen content. To each of five samples of the 200 mesh coal placed in test tubes, was added an excess of the Hanus iodine solution and the tubes were then sealed to prevent loss of iodine or bromine. After remaining in contact with the solution for different periods of time, the coal was filtered into a gooch crucible and thoroughly washed with warm glacial acetic acid until the washings showed no test for iodine with starch solution. The filtrate and washings were combined, an excess of a 10% solution of potassium iodide added, and the liberated iodine titrated with N/10 sodium thiosulphate solution.

Table V.-- The amount of iodine taken up by the coal when treated with an excess of Hanus iodine solution.

Sample	Wgt, of Sample	Time in Hours	c.c. N/10 $Na_2S_2O_3$ required	c.c. of N. iodine taken up	Iodine in grams	Percent	Oxygen Equiv. in grams
1	.5	24	6.85	1.0097	.1281	25.62	.00807
2	.5	48	6.25	1.072	.1361	27.22	.0085
3	.5	72	6.7	1.025	.1301	26.02	.0082
4	.5	96	6.7	1.025	.1301	26.02	.0082
5	.5	216	5.3	1.171	.1486	29.72	.0093
	10c.c.	216	16.55				

[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

II. The Treatment of Coal with Aqueous Bromine Solution.

In connection with the iodine treatment of coal, several determinations were made in an analogous manner using bromine solution instead of iodine. The concentration of the bromine solution was such that one cubic centimeter contained .00333 grams of bromine. After the coal had remained in the bromine water for two hours, it was filtered into a gooch crucible washed thoroughly with water and the bromine in the filtrate determined by adding potassium iodide in excess and titrating the liberated iodine. To determine the amount of bromine added, a blank was run using the same number of cubic centimeters of the solution as was added to the coal. The results are given in table VI.

Table VI.- The amount of bromine taken up when coal is treated with an aqueous bromine solution.

Sample	Wgt. of Sample	Time in Hours	Mesh	grams of Br added	grams iodine liberated	grams of Br taken up	Per Cent	" O " Equiv.
1	1	2	150	.5792	.0113	.5780	57.8	.0578
2	1	2	"	.5004	.0119	.4996	49.96	.0499
3	1	2	"	.5004	.0109	.4935	49.35	.0493
gas coke	.5	2	"	.6378	.5580	.2799	55.98	.0279
coke	.5	2	"	.6378	.6251	.2440	48.8	.0244

III. The Treatment of Coal with Potassium Dichromate Solution.

The coal used in these experiments was the same as that used in the iodine experiments. The coal was powdered to such degree

[illegible]

[illegible]

[illegible]

[illegible]

of fineness that it would pass through a 200 mesh sieve. To .5 gram samples were added 25cc. of N/10 $K_2Cr_2O_7$ and .5 cc. of dilute sulfuric acid. After standing in the dichromate solution for different periods of time, the coal was filtered into a gooch crucible, the bottom of which was covered with a round piece of filter paper. The coal was thorough ly washed with boiling water. To the filtrate and washings were added 10 cc. of a 15% solution of potassium iodide and 10 cc. of concentrated hydrochloric acid. The liberated iodine was titrated with standard $Na_2S_2O_3$. The coal together with the filter paper was transferred to a Parr Sulphur Fusion Cup and fused in the usual manner with sodium peroxide and potassium chlorate. The fusion was taken up with water, filtered from the iron and evaporated to dryness on the water bath. About 50 cc. of water were added to the residue, HCl added until strongly acid and the acid solution heated to boiling to make sure all of the hydrogen peroxide had been driven off. The solution was permitted to cool, potassium iodide added and the liberated iodine titrated with standard sodium thiosulphate solution.

The results obtained when coal is treated with Hanus iodine solution differ in degree only from those obtained with the aqueous solutions. When bromine solution is used instead of iodine the results, Table VI, show that the coal and gas coke take up practically the same percent of bromine. This too indicates that the absorption may be independent of the unsaturation. The action of $K_2Cr_2O_7$ on coal, like that of iodine and bromine, varies with the concentration and time of standing. The results, however, Tables VII and VIII, are not so marked as with the iodine and bromine. The results in table IX show the influence of temperature on the amount of $K_2Cr_2O_7$ reduced by the coal but do not give any additional information on the phenomena of adsorption.

The amounts of these various oxidizing substances taken up by the coal vary with the concentration of the oxidizing agent, the time of reacting, and the fineness of division of the coal. These are all phenomena which accompany that of adsorption. Then, too, if the assumption that coke contains no unsaturated compounds is correct, it would seem that coke should not take up as much iodine as does the coal. The fact that the gas coke takes up as much iodine and bromine as does the coal would indicate, therefore, that adsorption only is taking place. The other data, however, does not exclude the possibility that the action is one of adsorption together with oxidation.

Table VII.-- The amount of potassium dichromate reduced when coal is treated with N/10 $K_2Cr_2O_7$ solution.

Sample	Wgt, of Sample	Time in Days	Amount of N/10 solution added	N. c.c. of $K_2Cr_2O_7$ reduced	grams of $K_2Cr_2O_7$ reduced	chromium remaining in coal calculated as $K_2Cr_2O_7$	Difference	Oxygen Equiv. in grams
1	.5	10	25cc.	.6194	.0303	.0104	.0199	.00494
2	.5	11	"	.6662	.0327	.0127	.02	.00534
3	.5	12	"	.7026	.0345	.0107	.0238	.00563
4	.5	13	"	.6975	.0342	.0123	.0219	.00558
5	.5	14	"	.7172	.0351	.0123	.0228	.00573
6	.5	15	"	.7443	.0364	_	_	.00594
7	.5	17	"	.7443	.0364	.0131	.0233	.00594
8	.5	18	"	.7807	.0382	.0146	.0236	.00624
9	.5	19	"	.7391	.0362	_	_	.00591
10	.5	28	"	.8064	.0395	_	_	.00645

There was always a small amount of chromium remaining in the coal which could not be removed by washing with boiling water. The amount which was found in the coal after washing was determined as $K_2Cr_2O_7$ although there was no easy way of telling how much was in the form of chromium sulphate and how much was in the form of the dichromate. In any case the amount retained by the coal was never as great as the amount reduced as determined by titrating the filtrate, so the remainder must be accounted for as being used in the oxidation of the coal.

Further experiments were carried out using a .5 normal potassium dichromate solution instead of the N/10 solution. The following table shows that the number of normal cubic

ce

centimeters reduced to be much larger than in the case when N/10 solution was used.

Table VIII.--- The amount of potassium dichromate reduced when coal is treated with .5 N solution.

Sample	Weight of Sample	Time in Days	cc. of N/5 solution added	cc. of normal $K_2Cr_2O_7$ reduced	grams of $K_2Cr_2O_7$ reduced	Oxygen Equivalent in grams
1	.5	1	10	2.516	.1231	.0201
2	.5	3	10	3.027	.1483	.0242
3	.5	4	20	3.96	.1940	.0313
4	.5	5	20	4.23	.2072	.0338
5	.5	6	20	4.14	.2028	.0331

A few experiments were carried out to see what effect increase in temperature would have on the amount of $K_2Cr_2O_7$ reduced by the coal. The solution used was tenth normal. Five tenths gram samples were weighed and transferred to fiveglass stoppered bottles. Three of the samples were placed in a water bath maintained at a temperature of 46-53 ^{0}C. The other two were permitted to remain at room temperature. After the coal had remained in the solution for thirty six hours it was filtered and theamount of $K_2Cr_2O_7$ reduced was determined by titrating the filtrate in the usual way.

[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

Table IX.-- The effect of increase in temperature on the amount of $K_2Cr_2O_7$ reduced.

Sample	Weight of Sample	Temperature.	cc. N/10 $K_2Cr_2O_7$ added	cc, Normal $K_2Cr_2O_7$ reduced	grams of $K_2Cr_2O_7$ reduced	Oxygen Equiv. in grams
1	.5	46-53	25	1.96	.0960	.0156
2	.5	46-53	25	1.92	.0941	.0153
3	.5	46-53	25	2.02	.0989	.0161
4	.5	Room	25	1.12	.0548	.0089
5	.5	Room	25	1.08	.0529	.0086

An experiment was carried out to see what effect the treatment of coal with $K_2Cr_2O_7$ had on the calorific value. To five grams of 200 mesh coal was added 100cc. of .5 N $K_2Cr_2O_7$ and .5 cc. concentrated sulphuric acid. The coal was permitted to stand in the solution for four days. It was then filtered and thoroughly washed with hot water. After air drying for four days the moisture was determined by drying for an hour at 105^0 centigrade in the drying oven. The calorific values before treatment and after were determined by the Parr Oxygen Bomb Calorimeter.

	Amount of $K_2Cr_2O_7$ reduced per.gm.of coal	Moisture	B.T.U. per.gm. of dry coal
Original Coal		4.41	12,584
Coal treated with $K_2Cr_2O_7$	.1019 gms,	2.63	12,217

[illegible]

[illegible]

[illegible]

[illegible]

This is not enough data to draw any conclusions and owing to lack of time further work along this line could not be continued.

IV. The Treatment of Coal with Oxygen.

The experimental method of treating powdered coal with oxygen is described as follows:- The coal was powdered to 60 mesh and air dried. Between four and five grams were weighed in a glass weighing bottle. The weight was accurately noted and the bottle with the coal was placed in an oxygen bomb and oxygen admitted until a pressure of twenty five atmospheres had been obtained. After the coal had stood in contact with the oxygen at room temperature from four to five days, the oxygen was slowly allowed to escape by pressing the valve gently so as to avoid blowing the coal particles from the bottle. The bottle with its contents was then quickly weighed and the increase in weight carefully noted. The moisture content was determined before and after oxidation in order that the increase in weight could be calculated on the dry basis. The calorific value was determined before and after oxidation.

The effect of the oxygen on the coal was to produce an apparent decrease in the calorific value, but when the gain in weight was taken into consideration the calorific value was sometimes larger or equal to the calorific value of the original coal. As the data at hand was not sufficient to draw any general conclusions, it was thought advisable to omit it here. The question is indeed one which is open to more thorough investigation and as time was very short further work along this line had to be discontinued.

Summary.

I. The treatment of coal with iodine and bromine solutions.

The amounts of iodine or bromine taken up by a sample of fresh coal depend upon the following factors:- (1) the time the coal is allowed to remain in contact with the solutions; (2) the state of fineness which the coal has been powdered; and (3) the concentrations of the solutions. Since adsorption is dependent upon the above factors, state of fineness, time, and concentration of the solution, the reaction of coal with iodine or bromine solutions seems to be one of adsorption as well as of oxidation, substitution or addition.

II. The treatment of coal with potassium dichromate solutions.

Since the amount of chromium determined as $K_2Cr_2O_7$ retained by the coal after washing is always less than the amount reduced as determined by titration of the filtrate, the difference must be accounted for as being used in the oxidation of the coal.

III. Treatment of coal with oxygen under high pressure.

The results obtained by treating coal with oxygen under high pressure may be briefly summarized as follows:- (1) The coal in every case was found to increase in weight, and (2) Freshly mined coal took up more oxygen than coal which had stood in the laboratory for some time, and (3) The volume of oxygen absorbed by the coal was much greater at higher than at lower temperatures. (4) The effect of oxygen on the coal always produced an apparent decrease in the calorific value but when the gain in weight was considered, the calorific value of the oxidized coal was equal to or greater

than the original coal.

The treatment of coal with oxygen under high pressure for short intervals of time seem to produce the same effects with regards to increase in weight and calorific value as does weathering over long periods of time.

Review of Literature.

Dr, F. Hart (6) in Germany has carried out several experiments on the treatment of coal with iodine. Dr. Hart observed that in a large shipment of anthracite coal there appeared two kinds of coal, a glistening coal and a dull coal. Several samples of each were collected, powdered to 5000 mesh and treated with a Hübls iodine solution. Dr. Harts results are given in the following table:

Table I.

Sample	Weight of Sample	Kind of Coal	Grams of Iodine taken up
1	2 gm.	Shiny	.6235
2	"	"	.6195
3	"	"	.6055
4	"	"	.6091
5	"	Dull	.5287
6	"	"	.5671

The shiny coal contained 2.7% ash and the dull coal 7.35%. Therefore the amount of iodine absorbed calculated upon the

basis of 100 grams ash free coal was:-

Shiny --- 37.51 gm. of iodine

Dull --- 29.56 " " ""

Table II.

Kind of Coal	Weight of Sample	Grams of iodine absorbed	H_2O	vol.con.	Ash
English small	100gm.	23.68			
Bituminous	100 "	42.8			
Goudrow	100 "	30.54			
Dysart Main	100 "	30.96			
Dysart Fine	100 "	29.69			
Navigation	100 "	20.72	3.76	26.9	13.7
Arley	100 "	12.72	2.6	24.75	3.5

The following tables are taken from the work of Parr and Wheeler (7) showing the weight and the effect on heating value when coal is stored in bins in which it is exposed to weathering influences.

Table III.

Lab. No.	Description	Weight of coal dried at 105° C. in grams	Weight of coal dried at 105° C in grams	Gram gain in weight	Gain in weight per.cent
	Nut coal	Feb. 26.08.	Sept.16.08		
1219	Vermillion Co, Ill. Dry	947	960	13	1.37
1221	Sangamon CO.Ill	1196	1222	26	2.17
1223	Williamson " "	1138	1159	21	1.85

Table IV.

Vermillion County, Illinois, Nut Coal

Lab. No.	Sample taken	Dry Coal: Ash	Dry Coal: Sulphur	Dry Coal: B.T.U.	B.T.U. referred to unit coal	Decrease: B.T.U.	Decrease: per cent
1031	Same day as mined	10.55	4.25	12991	14814		
1081	7 days after mining	13.78	2.65	12412	14716	98	.66
1240	2 months after mining	14.21	2.47	12265	14577	237	1.60
1656	6 months after mining	13.53	2.10	12396	14575	239	1.61
		13.62	2.82	12282	14498	316	2.13

F.E.E. Lamplough and A. Muriel Hill in England have concluded that when coal dust is heated in an atmosphere rich in oxygen:-

(1) The heat evolved was nearly proportional to the volume of oxygen absorbed, the mean value being 3.3 calories of heat produced brought about by the absorption of one cubic centimeter of oxygen.

(2) The production of heat may be attributed to two chemical changes, the oxidation of iron pyrites and the oxidation of carbonaceous matter.

(3) The oxidation of carbonaceous matter in coals practically free from iron was not so rapid as in those containing much iron, but continued for a long time comparatively little carbon dioxide being evolved so that eventually there was considerable evolution of heat even in the absence of ventilation.

(4) Oxidation of coal dust takes place in contact with gas containing much less than the normal proportion of oxygen present in air.

(5) The oxidation of carbonaceous matter and the total changes occuring in pyrites during the absorption of a given volume of oxygen produce about the same amount of heat, so that the rate at which heat is given off in the oxidation of coal dust due to either process may with suprising nearness be determined by the volume of oxygen absorbed.

Bibliography.

1. Trans. INST. Min. Eng. 45, 629 1912-13

2. Univ. Ill. Bull. No.38 1909.

3. U.S. Bur. Mines Bull. 29

4. Tech. Paper 65 U.S. Bur. Mines

5. Chemiker Zeitung 97- 1204 - 1906

6. Chemiker Zeitung 97- 1204,- 1906

7. Univ. of Ill. Bull. 38 - 1909.